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FIFTH QUARTERLY REPORT

STUDY & DETERMINATION OF AN OPTIMUM DESIGN FOR SPACE UTILIZED LITHIUM DOPED SOLAR CELLS

15 October 1970

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Contract 952554

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TRW Systems Group
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I. LITHIUM DOPED SOLAR CELL EVALUATION

During the past quarter, lithium doped solar cells from Centralab and Heliotek have been irradiated with 1 MeV electrons and their recovery characteristics have been studied. Several different processing experiments were represented in these cells, including different diffusion gases and varying percent of lithium coverage of the rear surface. The groups that were evaluated, C11A through C11D, H1A, H2A, H4A, H5A1, H5A2 and H5A3, are listed, along with their material and processing variables, in Table I.

All of the cells received radiation exposure to 1 MeV electrons. Tungsten I-V characteristics and capacitance versus voltage measurements were then obtained as a function of time at either room temperature or 60°C. The general radiation damage and recovery characteristics of each cell group are summarized in Tables II and III. The recovered levels given in the tables are the peak of the recovery curve and do not take into account any redegradation that may have occurred.

The one-half recovery time is the time necessary for short circuit current to reach a point midway between the damaged level and the peak recovered level. In general it can be observed that the higher lithium concentrations results in lower initial characteristics, higher recovered levels, and more rapid annealing rates while with lower lithium concentrations, higher initial and slower recovery rates exist. In Table IV, the peak recovered levels are compared graphically with each other and with the equivalent damage level for both contemporary 10 Ω-cm n/p cell and the best previous float zone and crucible groups. The spread in the data and the half recovery time are also shown. It should be noted that most cell groups tested were superior to the contemporary n/p cells in recovered level. The initial short circuit current of most of the cells being reported on was inferior to the contemporary n/p cells.

A. Centralab Cells

The Centralab cells submitted for evaluation were all fabricated from quartz crucible grown silicon, with the exception of group (C11C). The variable of boron dopant gas was investigated by diffusing the p-type front surface with boron trichloride in the case of group C11A and boron tribromide in the case of group C11B. The results of this evaluation can be seen in Figures 1 and 2. The short circuit current values of cells received in group C11B were rather low (53 ma) compared to that group C11A. This difference is not believed to be related to the use of boron tribromide. It is known that when Texas Instruments manufactured solar cells, their p-type diffusions were made with boron tribromide. A second important difference between the cells of these two groups is concentration of lithium found at the junction. Although the cells of both C11A and C11B groups were lithium diffused in the same manner (480 min. at 325°C), the data in Table III indicates that group C11A contains twice the lithium concentration of group C11B. This difference is not considered to be related to use of boron tribromide. The effect of this lower lithium concentration can be seen in the 60°C recovery data in Figures 1 and 2. The cells of group C11A are nearly fully recovered 200 hours after irradiation, however, those of C11B appear to be only half recovered at a comparable recovery time. This slower recovery is probably due to the lower lithium concentration. The recovered I_{sc} values of the C11A group cells are 38 ma after irradiation of $3x10^{15}e/cm^2$. The value is significantly better the comparable fata for conventional n/p cells. Recovery in the C11B group has not progressed sufficiently to determine final recovered I_{sc} value.

The cells of group C11D were lithium diffused at the slightly higher temperature of 375°C for 180 minutes. This diffusion schedule resulted in a higher concentration of lithium at the junction. These cells have about $5x10^{14}$ lithium atoms/cm^3. The C11A cells diffused at 325°C for 480 min. (C11A) had only $3x10^{14}$ Li/cm^3. It is also noted that slope of the log capacitance versus log voltage is -0.26. This is the lowest value found in the current group of cell under evaluation. The high lithium concentrations in group C11D are reflected in a slightly more rapid recovery after irradiation. The initial I_{sc} values of the cells in groups C11A and C11D are comparable with those of conventional n/p solar cells. The cells of groups C11A, C11B, and C11D are interesting in that they have the lowest lithium concentrations of any quartz crucible silicon cell evaluated by TRW. The relatively poor performance of cells in group C11B, indicate that for this type of cell, the concentration of lithium at the junction should be kept above $2x10^{14}/cm^3$.

The remaining Centralab group, C11C, was fabricated from Lopex (low oxygen, low dislocation) silicon. In general the performance of the group was very good. The cells were lithium diffused at 325°C for 480 minutes. The resulting lithium concentration in this group was $1.5x10^{14}/cm^3$. The results of the $3x10^{14}e/cm^2$ and $3x10^{15}e/cm^2$ radiations are shown in Figures 4 and 5. In both cases, the I_{sc} recovered to values greater than those of comparably irradiated n/p solar cells, as shown by the dashed lines on these graphs. Although the recovery kinetics are relatively slow in these cells, due to the lower lithium concentration, the irradiated cell performance is among the best received to date.

B. Heliotek Cells

All Heliotek cells received for evaluation during the past quarter were fabricated from either floating zone or Lopex silicon and, therefore, had lower oxygen concentrations. There are two different experimental variables represented in these Heliotek cells. Two groups (H1A and H4A) were diffused at lower temperatures. A 325°C lithium diffusion for 480 minutes. Group H2A was lithium diffused at 425°C for 90 minutes with a 120 minute redistribution cycle. This latter diffusion schedule has been used extensively in the past and can be regarded as control. The capacitance measurements results from the H1A group, shown in Table II, indicate that very little or no lithium reached the junction. For this reason the irradiation recovery results shown in Figures 6 and 7 are very poor. Although some recovery is observed after $3x10^{14}e/cm^2$, the higher fluence of $3x10^{15}e/cm^2$ exhausts the lithium and no recovery is observed. These results are in direct conflict with those for group H4A which had an identical history. The H4A cells had approximately $5x10^{14}$ lithium atoms/cm^3 at the junction, and exhibited satisfactory recovery as shown in Figures 8 and 9. The recovered I_{sc} values of the H4A cell would probbably have been higher if the before irradiation I_{sc} values had been higher than 46 ma. This condition is not necessarily a result of the lithium diffusion, as other cells with similar lithium concentrations have initial I_{sc} values in excess of 60 ma. Despite this difficulty, the data in Figure 9 indicated that cells of group H4A recover to I_{sc} values of 40 ma after a fluence of $3x10^{15}e/cm^2$. This is considerably higher than a comparable irradiated n/p solar cell

The irradiation recovery results for the cells of group H2A are shown in Figures 10 and 11. As mentioned previously, this lithium diffusion schedule has previously been used many times to produce superior lithium cells. The results in Figure 10 and 11 confirm that such cells exhibit excellent I_{sc} values when recovered from an irradiation. The results in the case of the $3x10^{15}e/cm^2$ fluence are particularly interesting in that the recovered I_{sc} reached a value of 44 ma. The fact that these cell were fabricated from Lopex silicon as opposed to float zone silicon is not considered significant.

The remaining groups of Heliotek cells represent a series of experiments to determine the effectiveness of area coverage during the application of lithium diffusion source material to the back of the cell. Groups H5A1, H5A2, and H5A3, respectively received 100%, 80% and 50% back surface area coverage. The results of this experiment are very interesting for comparative analysis. The first point of interest is the measured lithium concentrations at the junctions of the various groups as seen in Tables II and III. The cells with 100% coverage (H5A1) have approximately $6x10^{14}$ lithium atoms/cm^2 at the junction. The groups which received less coverage (H5A2, H5A3) had roughly half the above lithium concentration. The results indicate quite clearly that decreased area coverage reduces the concentration of lithium at the junction. The relationship does not appear to be linear, since the cells with 80% coverage (H5A2) have lithium concentrations nearly as low as those with 50% (H5A3). It can be concluded that incomplete area coverage with the lithium source material significantly reduces the lithium concentration at the junction. It is also of interest to compare the cells of these groups to cells of other groups. The cells of group H2A were made with the same material and diffusion schedule, but presumably no control on area coverage. The data in Tables I and II indicate the H2A cells had much lower lithium concentrations than any of the cells in H5 groups. It must be concluded that there are other unknown factors which extend strong influences on the concentration of lithium reaching the junction. One possible factor could be the chemical activity of the lithium in the source material.

The effects of various lithium source area coverages on radiation response can be seen in Figures 12 through 17. The initial I_{sc} values of these cells are all relatively low. The values average approximately 51 ma. This parameter influences radiation recovery behavior, because the maximum recovered parameters can only approach and not exceed their initial values. Despite this problem, the cells of group H5A1 (100% coverage) recovered to a maximum I_{sc} of 50 ma after an irradiation of $3x10^{14}e/cm^2$ and 39 ma after $3x10^{15}e/cm^2$. In both cases these values are above those of similarly irradiated conventional n/p solar cells. In Figure 12, the H5A1 cells, irradiated with $3x10^{14}e/cm^2$, show some redegradation of I_{sc} after the maximum was reached. The radiation recovery of cells of group H5A2 (80% coverage) was not drastically altered by the reduced coverage. In Figure 14, it can be seen that the cells of group H5A2 which were irradiated with $3x10^{14}e/cm^3$ recovered to I_{sc} values of 45 ma. The recovery probably would have exceeded the above value if the initial I_{sc} value had been greater than 46 ma. The results of the $3x10^{15}e/cm^2$ irradiation of H5A2 cell (Figure 15) indicates I_{sc} recovery to 39 ma after irradiation. This value is equal to that achieved in the group having 100% coverage (H5A1). This result is difficult to explain condidering the lower lithium concentration and the studies of D. L. Kendall at Texas Instruments of which indicated very little lateral spreading of lithium during diffusion. The results for cells of H5A3 (50% coverage) show comparable performance after $3x10^{14}e/cm^2$ (Figure 16). In the case of the higher electron fluence (Figure 17) the H5A3 cell recovered I_{sc} values significantly reduced. It appears that incomplete coverage with diffusion source material does not reduce recovery behavior, except in extreme cases.

II. KINETICS OF LITHIUM IN SILICON

Work has been re-initiated on the evaluation of p-type lithium counterdoped silicon for use in solar cells. This effort is being directed in several areas. Studies on bulk silicon are in progress through Hall coefficient evaluation, transient photoconductivity, and metal-semiconductor test diodes. In addition n+ on p diffused structures are being fabricated for evaluation of techniques for lithium counterdoping in solar cells. The Hall coefficient work has shown that the lithium counterdoped silicon has an extremely small carrier removal rate under very high 1 MeV electron fluences. The lower removal rate is interpreted as a probable reaction of lithium with radiation produced complexes. Although this behavior is of secondary interest, it indicates a similar possibility for radiation produced recombination centers. We are currently in the process of making suitable test diodes for minority carrier diffusion length evaluation of radiation damage for the lithium counterdoped material.

III. PROGRESS IN THE NEXT REPORT PERIOD

During the next report period the irradiation of JPL-furnished solar cells will be continued. Capacitance measurements made on cells irradiated will be analyzed to allow a thorough study of the lithium concentration changes which occur during irradiation and recovery. The study of p-type lithium counter doped devices will be started to investigate possible radiations hardness benefits.

IV. NEW TECHNOLOGY

There is no new technology reported in this paper.

V. PAPERS AND PUBLICATIONS GENERATED

Accepted for Publication

Title: "Effect of Electron Irradiation on Lithium Doped Silicon"
Journal: International Journal of Physics and Chemistry of Solids

Presented

Title: "Role of Lithium in Irradiated Solar Cells"
Meeting: International Colloquium on Solar Cells, Toulouse, France, 6 July 1970.

Title: "Role of Lithium in Irradiated Solar Cell Behavior"
Meeting: Eighth Photovollaic Specialists Conference, Seattle, Washington, 11 August 1970.

Submitted

Title: "Role of Lithium in Irradiated Solar Cell Behavior"
Journal: Energy Conversion

BASE MATERIAL			LITHIUM INTRODUCTION		
Cell Group	Mat'l Type	Resistivity Ω-cm	Diffusion Schedule °C/Min/Min	Average Li. Conc. @ Junction Cm^{-3}	Remarks
C11A	Cruc	45	325/480/0	$3.1x10^{14}$	BCl_3 Tackon
C11B	Cruc	45	325/480/0	$1.5x10^{14}$	BBr_3 Diffused
C11C	Lopex	75	325/480/0	$1.5x10^{14}$	BCl_3 Tackon
C11D	Cruc	45	375/180/0	$5.1x10^{14}$	BCl_3 Tackon
H1A	F.Z.	20	325/480/0	0	(1st set of low temp.)
H2A	Lopex	20	425/90/120	$1.6x10^{14}$	
H4A	F.Z.	20	325/480/0	$5.2x10^{14}$	(2nd set of low temp.)
H5A1	Lopex	20	425/90/120	$5.7x10^{14}$	100% Li-REAR
H5A2	Lopex	20	425/90/120	$3.6x10^{14}$	80% Li-REAR
H5A3	Lopex	20	425/90/120	$3.1x10^{14}$	50% Li-REAR

TABLE I - LITHIUM SOLAR CELL MANUFACTURING PARAMETERS

Cell Group	Diffusion Schedule °C/Min/Min	N_{Li} cm^{-3}	Average C vs V Slope	Electron Fluence e/cm^2, 1 MeV	Initial Level I_{SC}, mA	Damaged Level I_{SC}, mA	Recovered Level I_{SC}, mA	Time (hrs.) to 1/2 Recovery Pt. @ 25°C
C11C	325/480/0	$1.1x10^{14}$	-.37	$3x10^{14}$	60.3	34	54	50
H1A	325/480/0	0	-.47	$3x10^{14}$	58	33	45	100
H2A	425/90/120	$.4x10^{14}$	-.32	$3x10^{14}$	51	31	48	5
H4A	325/480/0	$4.9x10^{14}$	-.35	$3x10^{14}$	47	27	46	3
H5A1	425/90/120	$4.2x10^{14}$	-.34	$3x10^{14}$	52.5	27	50	3
H5A2	425/90/120	$2.8x10^{14}$	-.34	$3x10^{14}$	46.5	27	45.5	3
H5A3	425/90/120	$2.3x10^{14}$	-.36	$3x10^{14}$	52.0	27	47	3 1/2
C11C	325/480/0	$1.9x10^{14}$	-.34	$3x10^{15}$	58.5	24.3	39	50
H1A	325/480/0	0	-.47	$3x10^{15}$	56	24	25	
H2A	425/90/120	$2.7x10^{14}$	-.30	$3x10^{15}$	56	22	44	15
H4A	325/480/0	$5.6x10^{14}$	-.33	$3x10^{15}$	46	19.5	40	14
H5A1	425/90/120	$8.5x10^{14}$	-.32	$3x10^{15}$	47.5	17.2	39	50
H5A2	425/90/120	$4.4x10^{14}$	-.35	$3x10^{15}$	51	19	39	25
H5A3	425/90/120	$3.8x10^{14}$	-.36	$3x10^{15}$	53.	18	33	15-100

TABLE II - FLOAT ZONE SILICON CELL RECOVERY CHARACTERISTICS

Cell Group	Diffusion Schedule °C/Min/Min	N_{Li} cm^{-3}	Average C vs V Slope	Initial Level I_{SC}, mA	Damaged Level I_{SC}, mA	Recovered Level I_{SC}, mA	Time (hrs.) to 1/2 Recovery Pt. @ 60°C
C11A	325/480/0	3.1×10^{14}	-.28	64.2	22.0	>37	50-100
C11B	325/480/0	1.5×10^{14}	-.32	53.3	24.9	>27	>100
C11D	375/180/0	5.1×10^{14}	-.26	61.5	20.7	>36	50

TABLE III - CRUCIBLE LITHIUM SOLAR CELL RECOVERY CHARACTERISTICS AFTER 60°C 3×10^{15} e/cm^2, 1 MeV

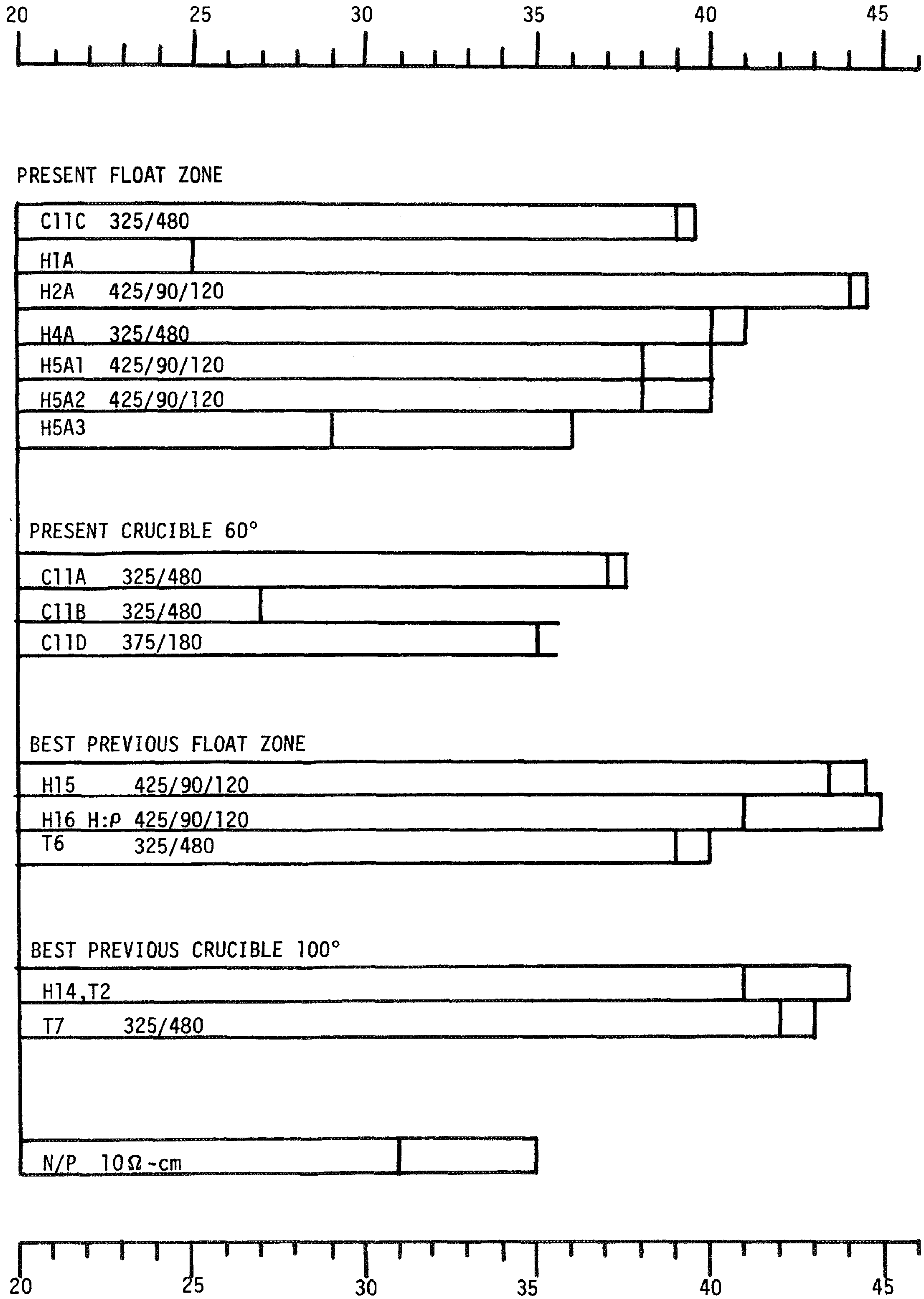

TABLE IV - COMPARISON OF PEAK RECOVERED LEVELS (I_{SC}-TUNGSTEN)

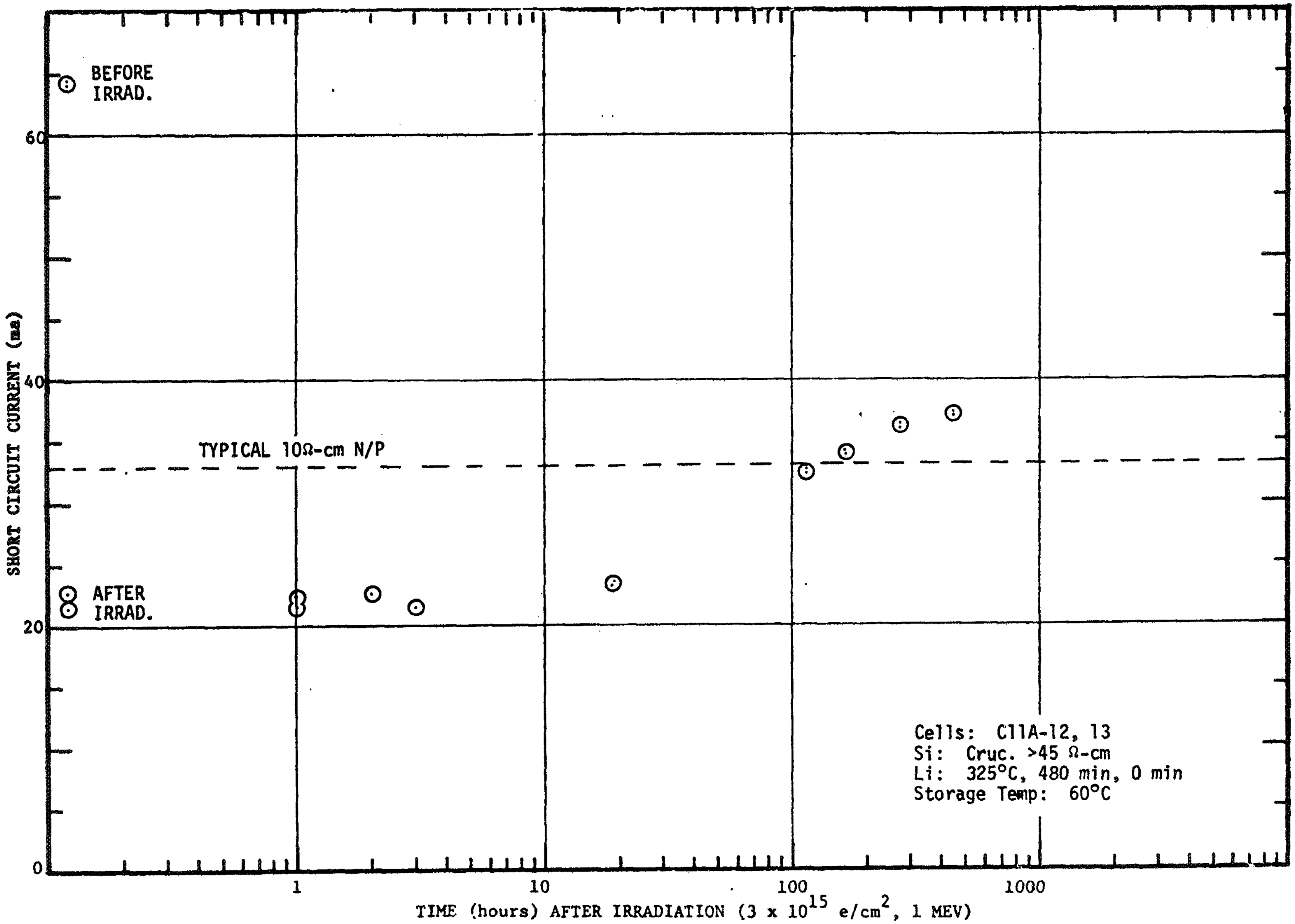

FIGURE 1 - RECOVERY OF GROUP C11A SOLAR CELLS, 3×10^{15} e/cm^2

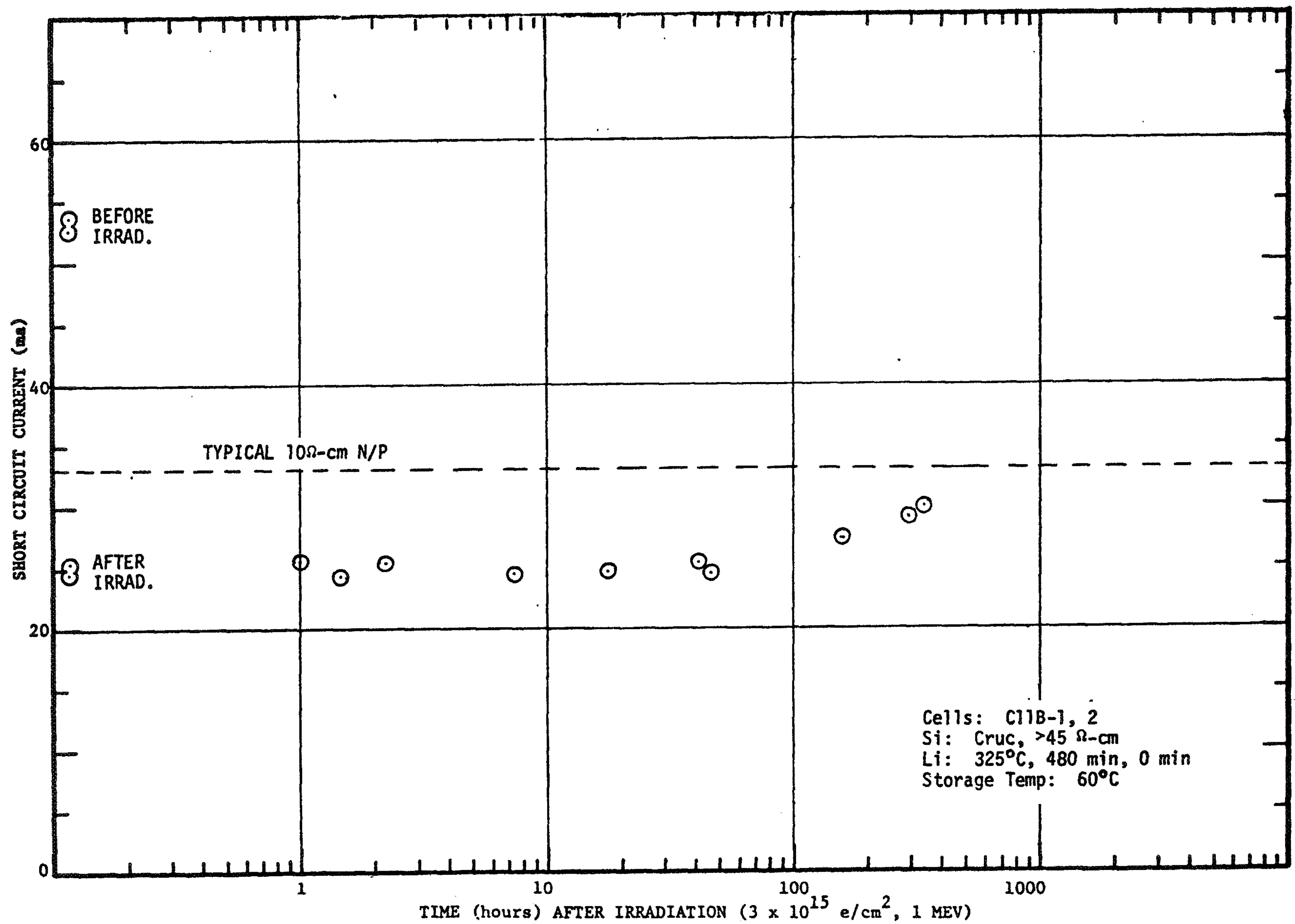

FIGURE 2 - RECOVERY OF GROUP C11B SOLAR CELLS, 3×10^{15} e/cm^2

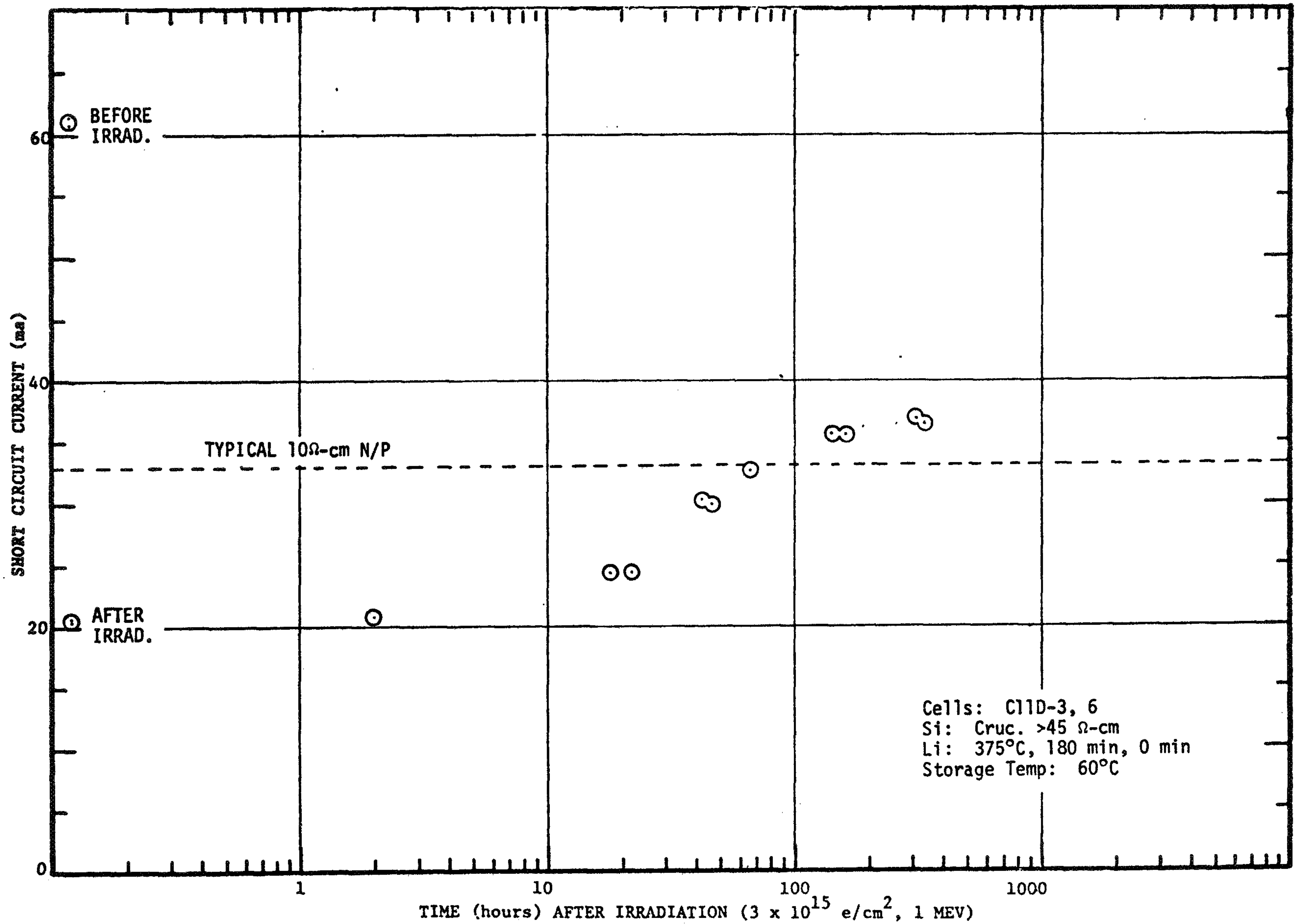

FIGURE 3 - RECOVERY OF GROUP C11D SOLAR CELLS, 3×10^{15} e/cm^2

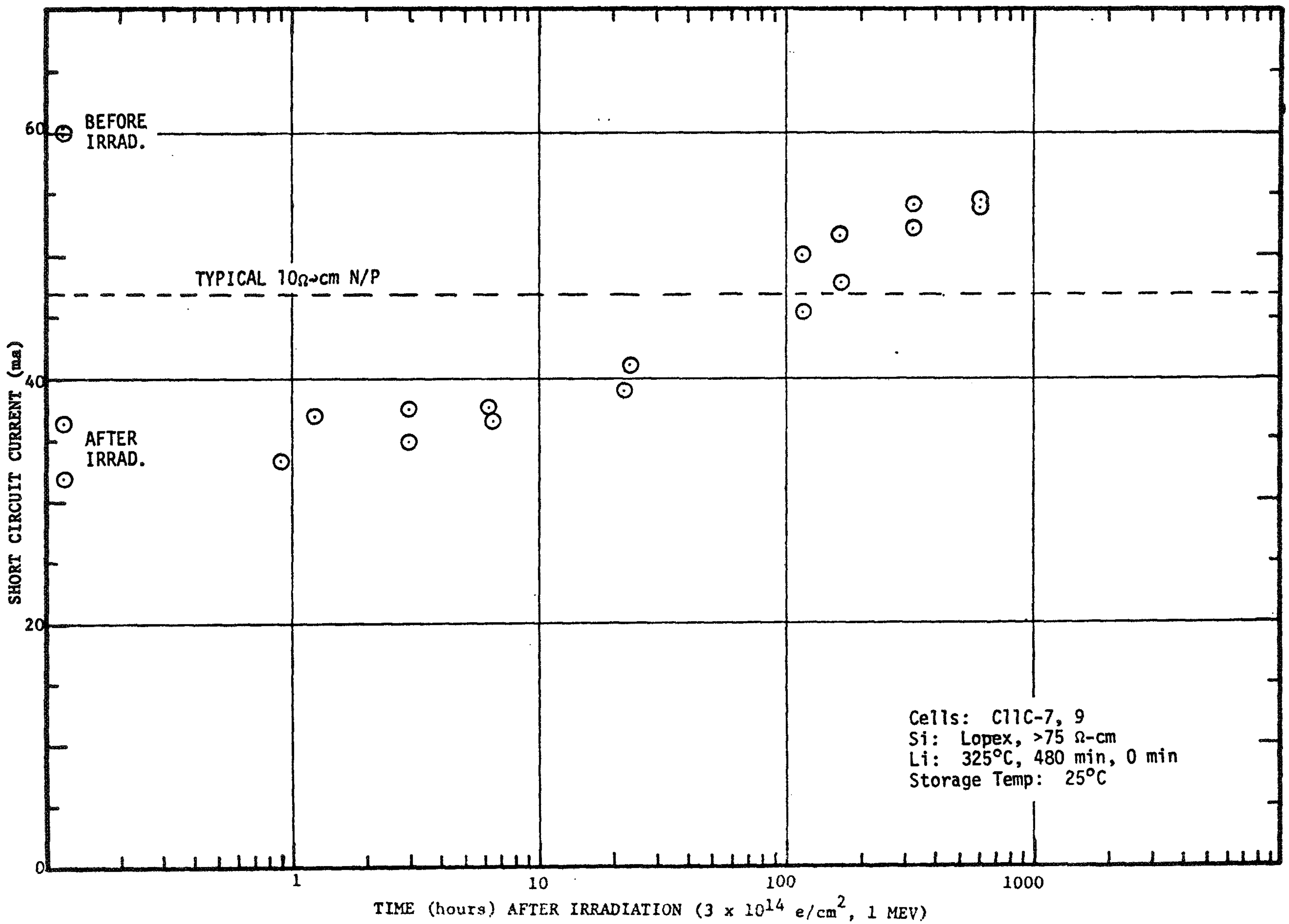

FIGURE 4 - RECOVERY OF GROUP C11C SOLAR CELLS, 3×10^{14} e/cm^2

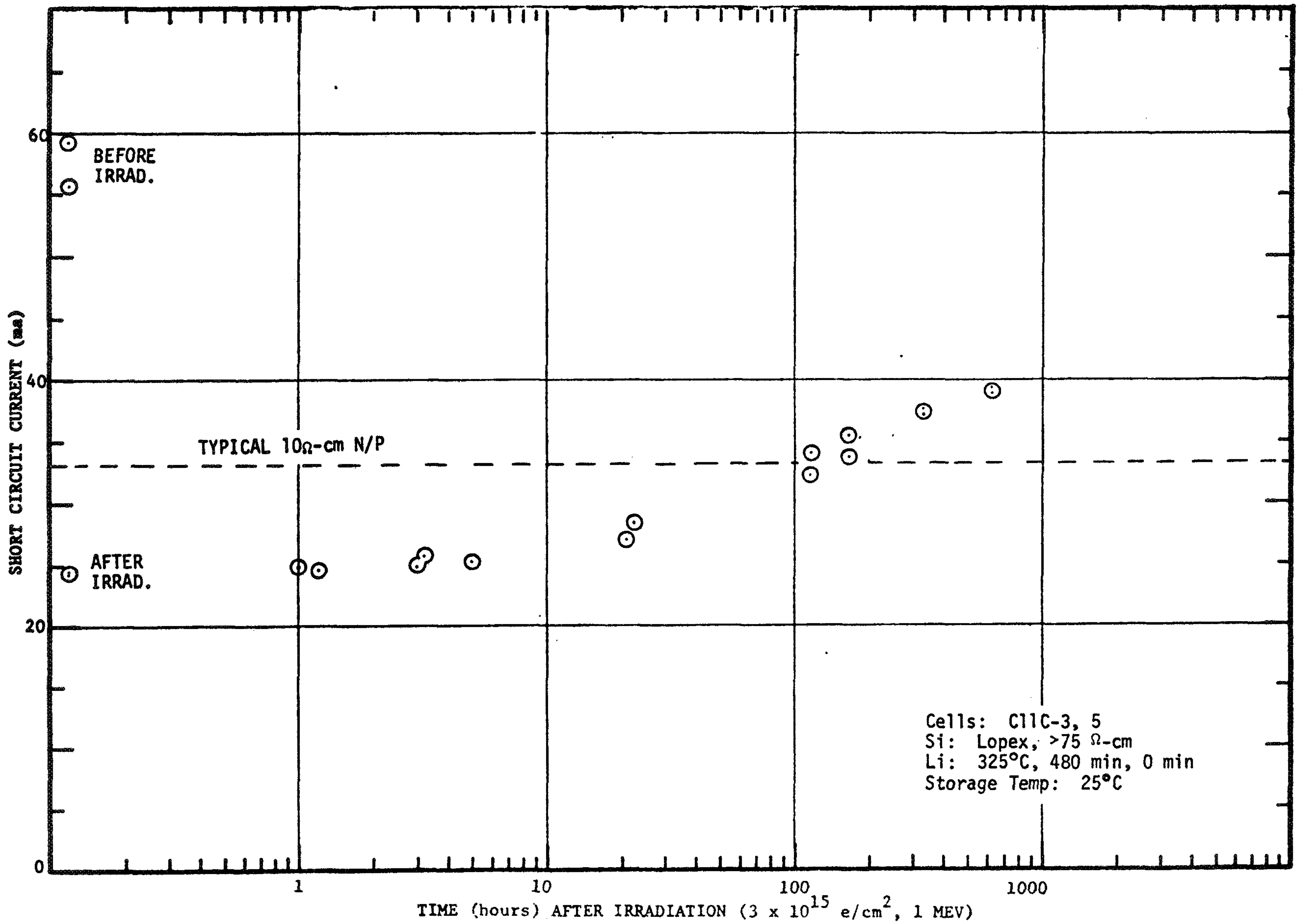

FIGURE 5 - RECOVERY OF GROUP C11C SOLAR CELLS, 3×10^{15} e/cm^2

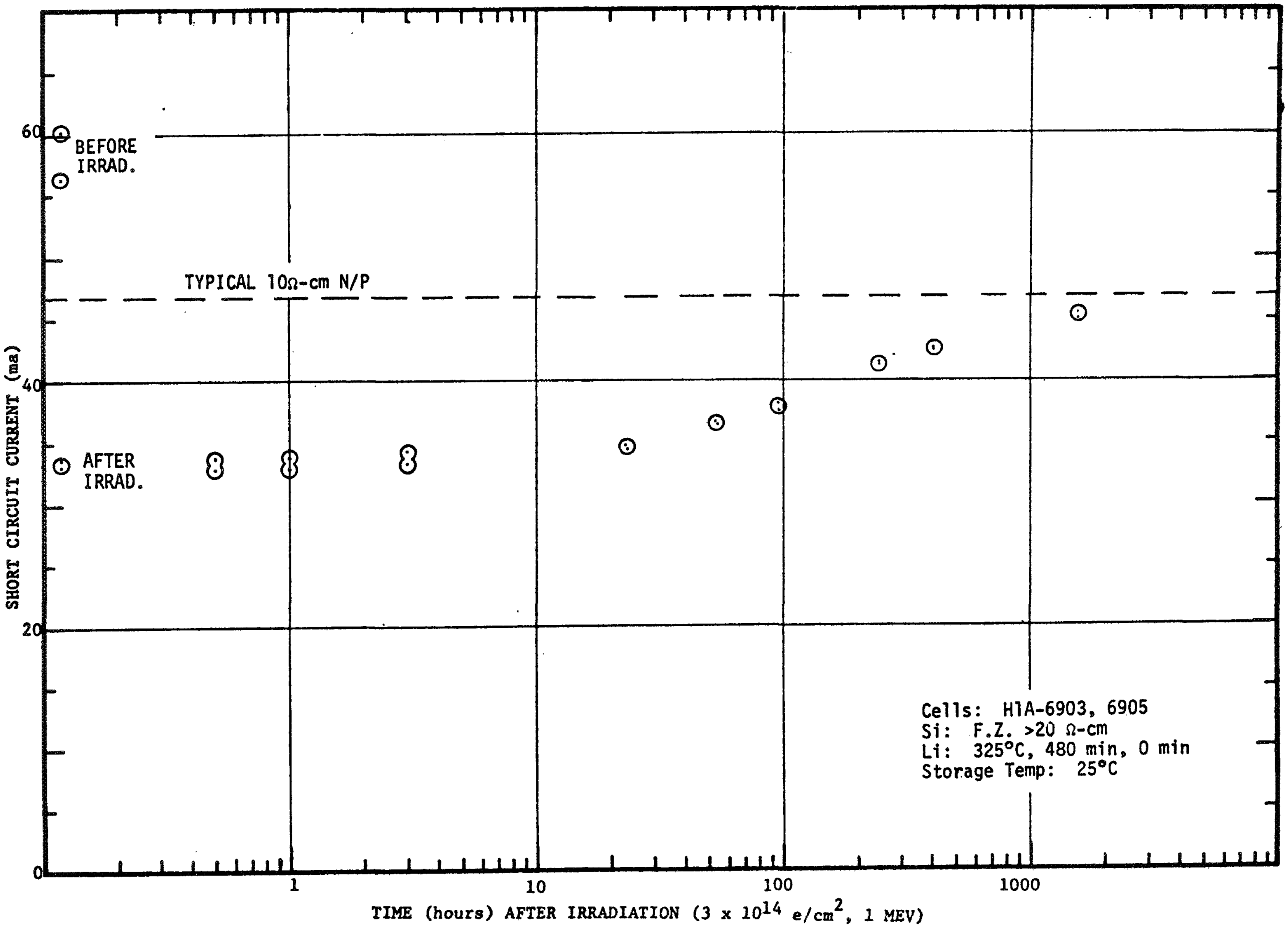

FIGURE 6 - RECOVERY OF GROUP H1A SOLAR CELLS, 3×10^{14} e/cm^2

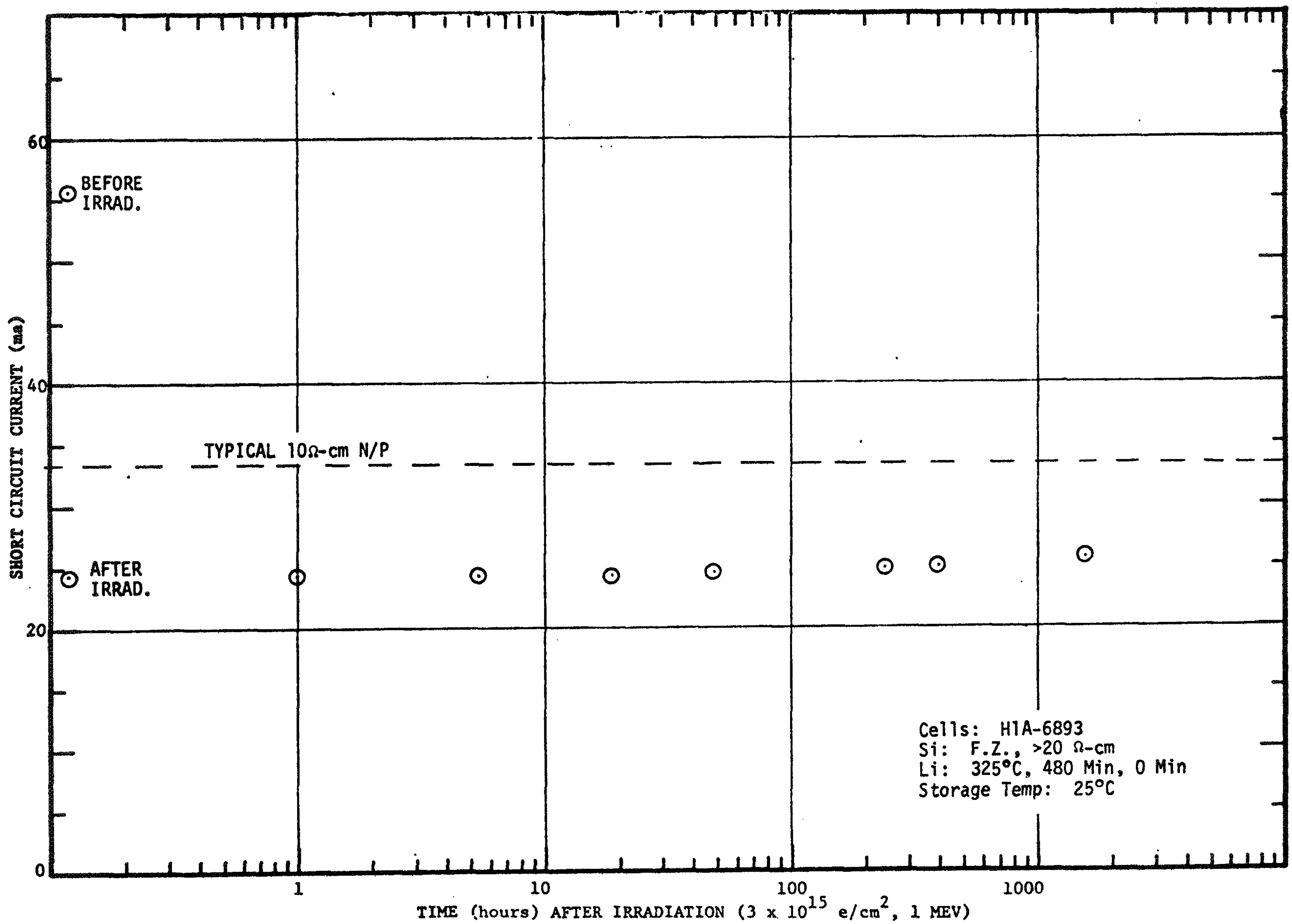

FIGURE 7 - RECOVERY OF GROUP H1A SOLAR CELLS, 3×10^{15} e/cm^2

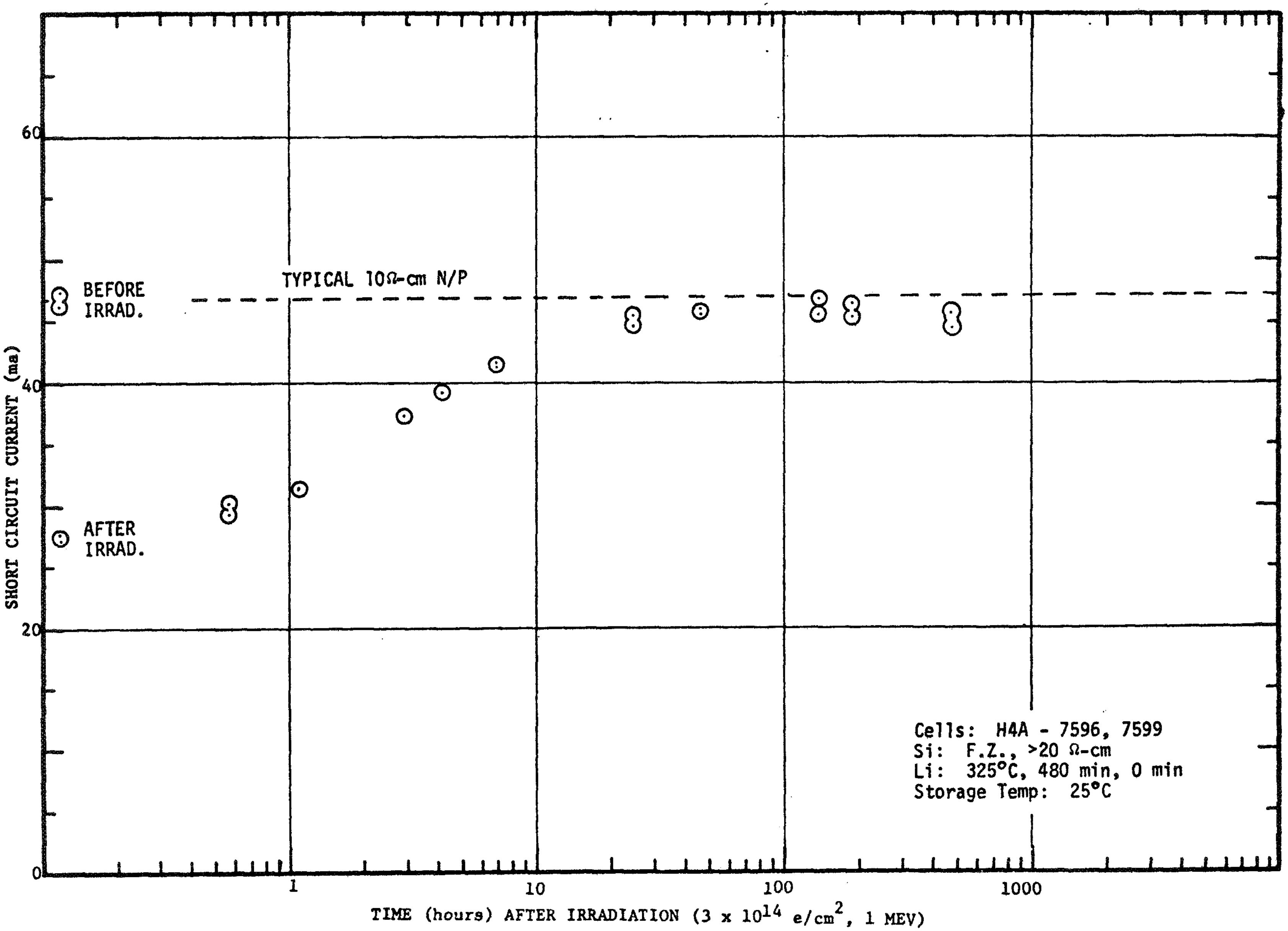

FIGURE 8 - RECOVERY OF GROUP H4A SOLAR CELLS, 3×10^{14} e/cm^2

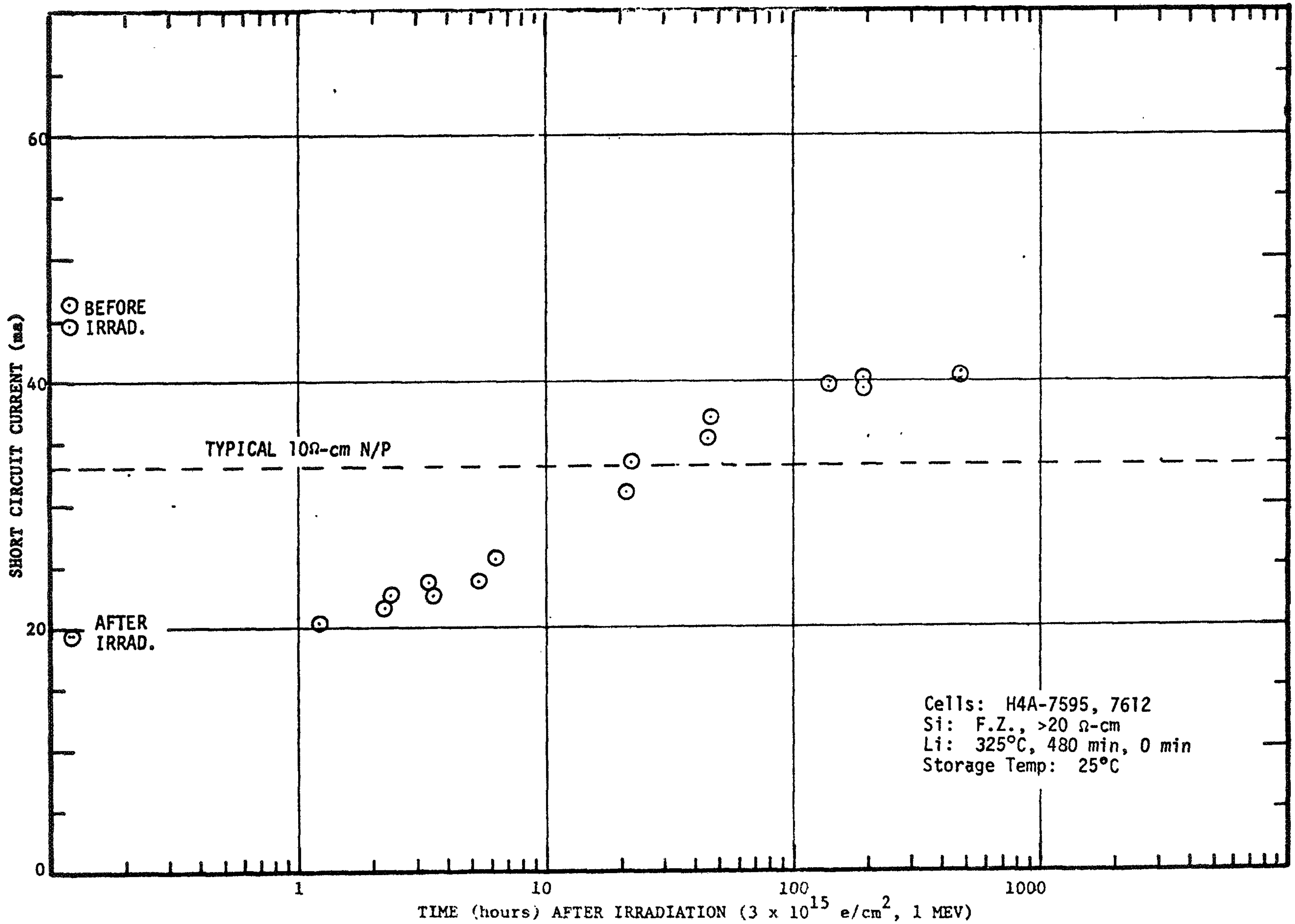

FIGURE 9 - RECOVERY OF GROUP H4A SOLAR CELLS, 3×10^{15} e/cm^2

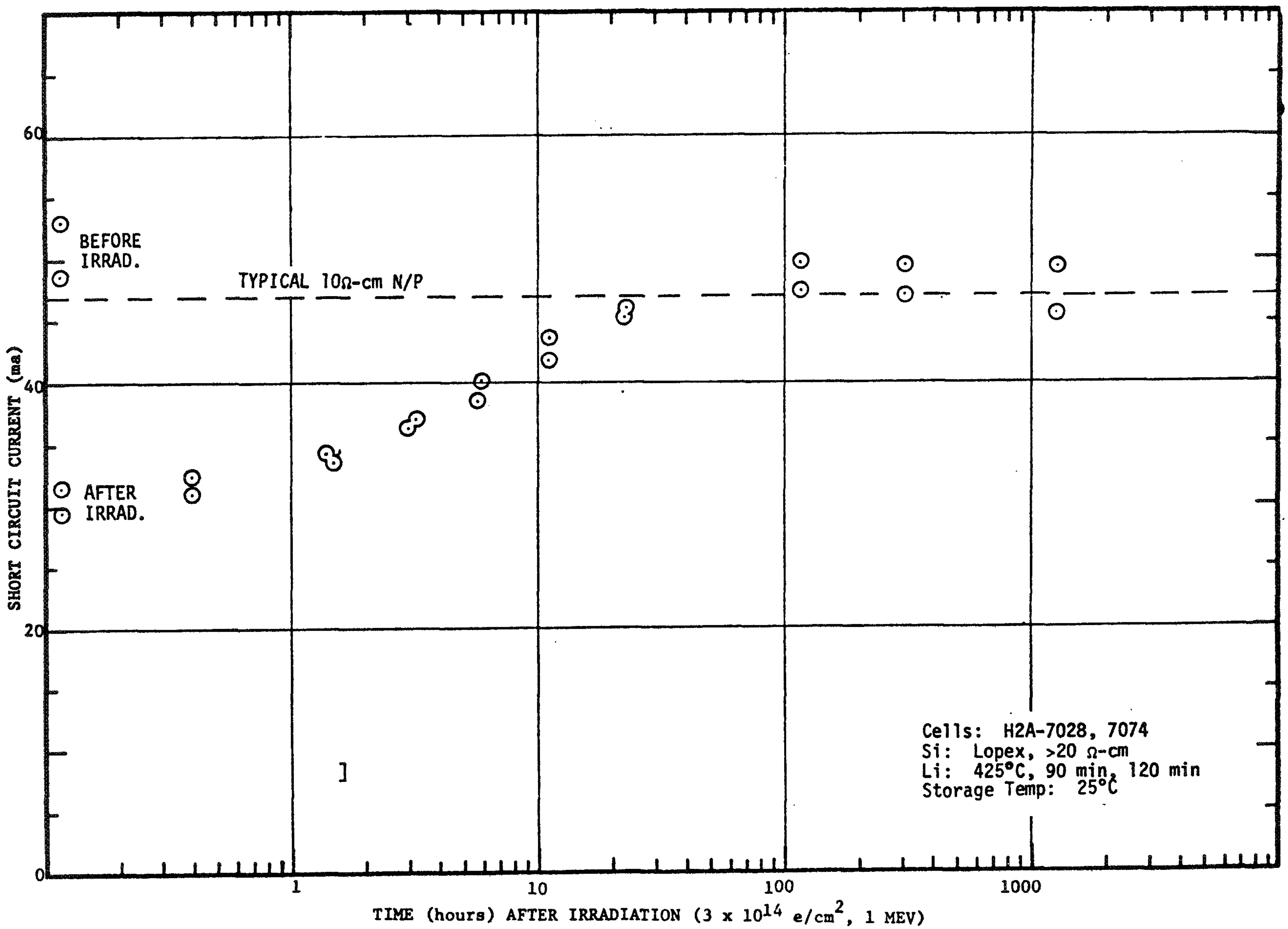

FIGURE 10 - RECOVERY OF GROUP H2A SOLAR CELLS, 3×10^{14} e/cm^2

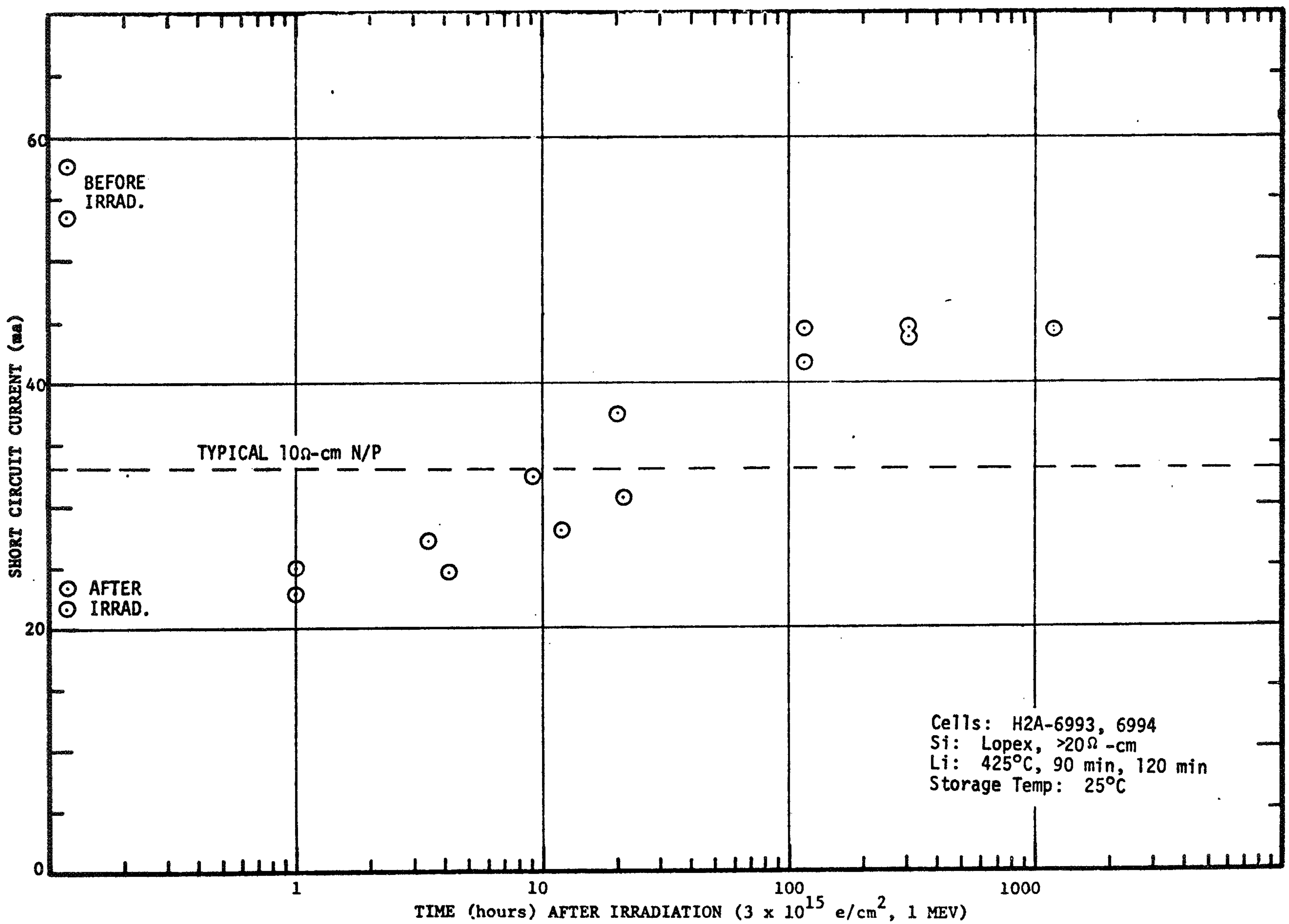

FIGURE 11 - RECOVERY OF GROUP H2A SOLAR CELLS, $3x10^{15}$ e/cm^2

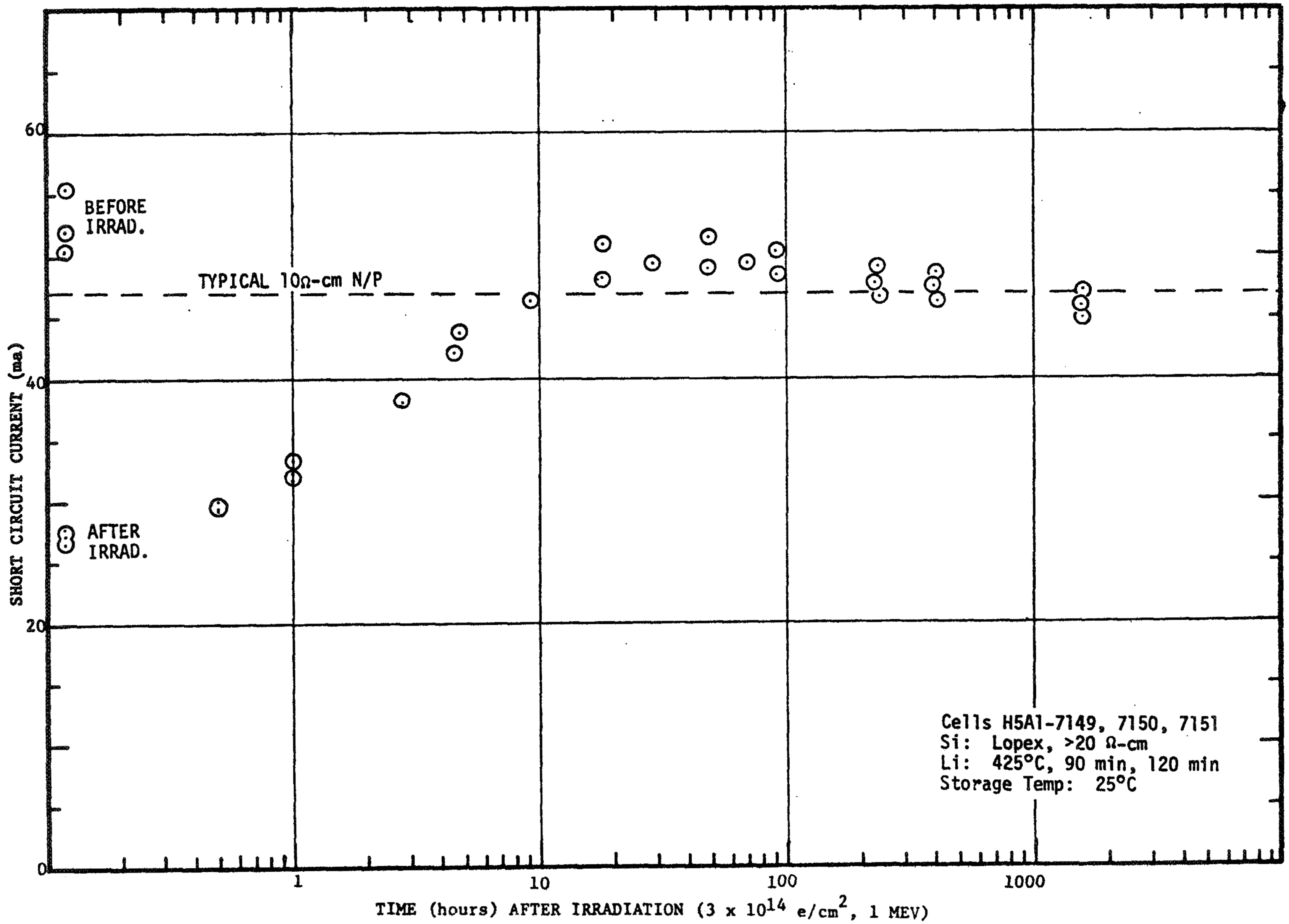

FIGURE 12 - RECOVERY OF GROUP H5A1 SOLAR CELLS, 3×10^{14} e/cm^2

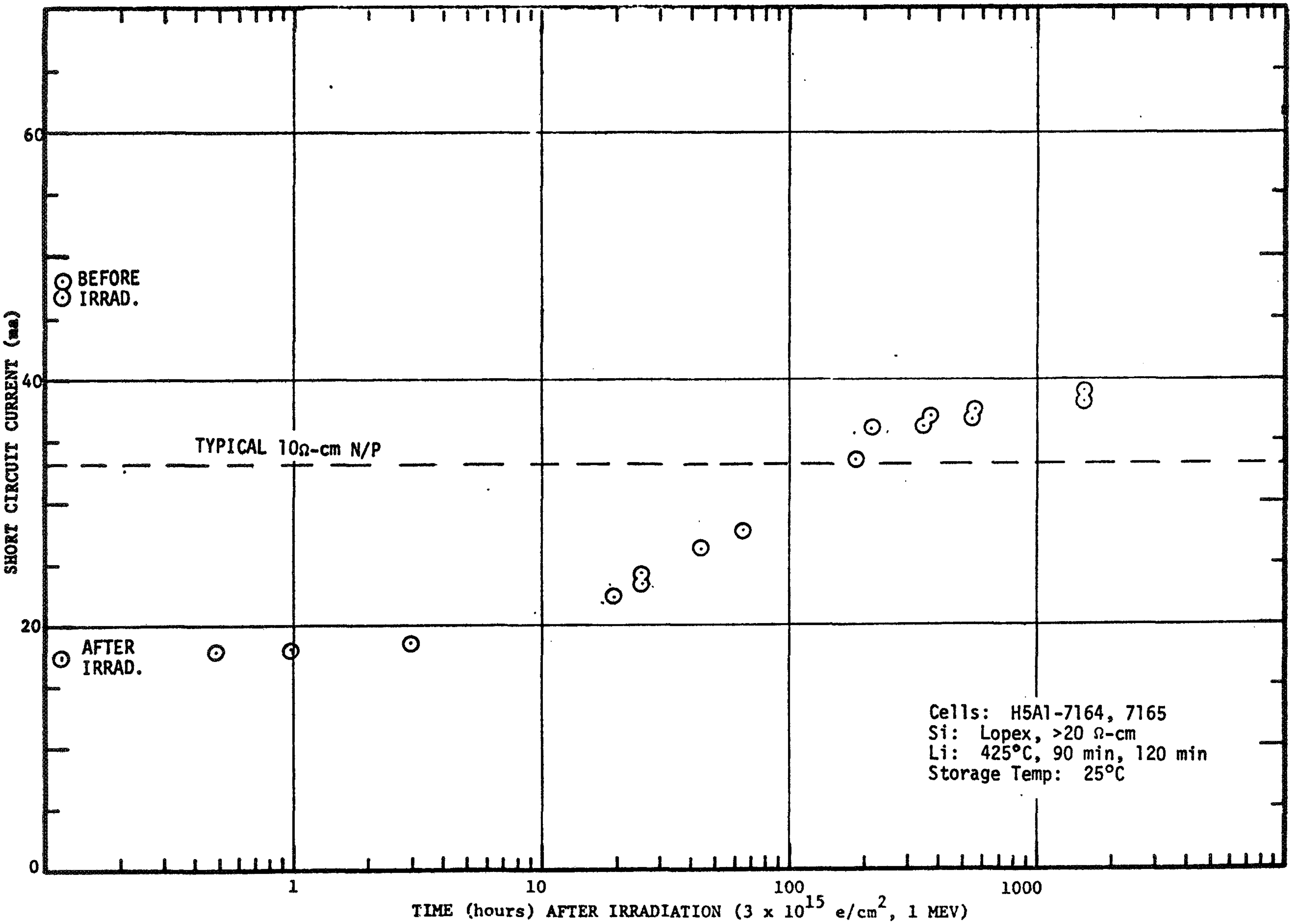

FIGURE 13 - RECOVERY OF GROUP H5A1 SOLAR CELLS, 3×10^{15} e/cm^2

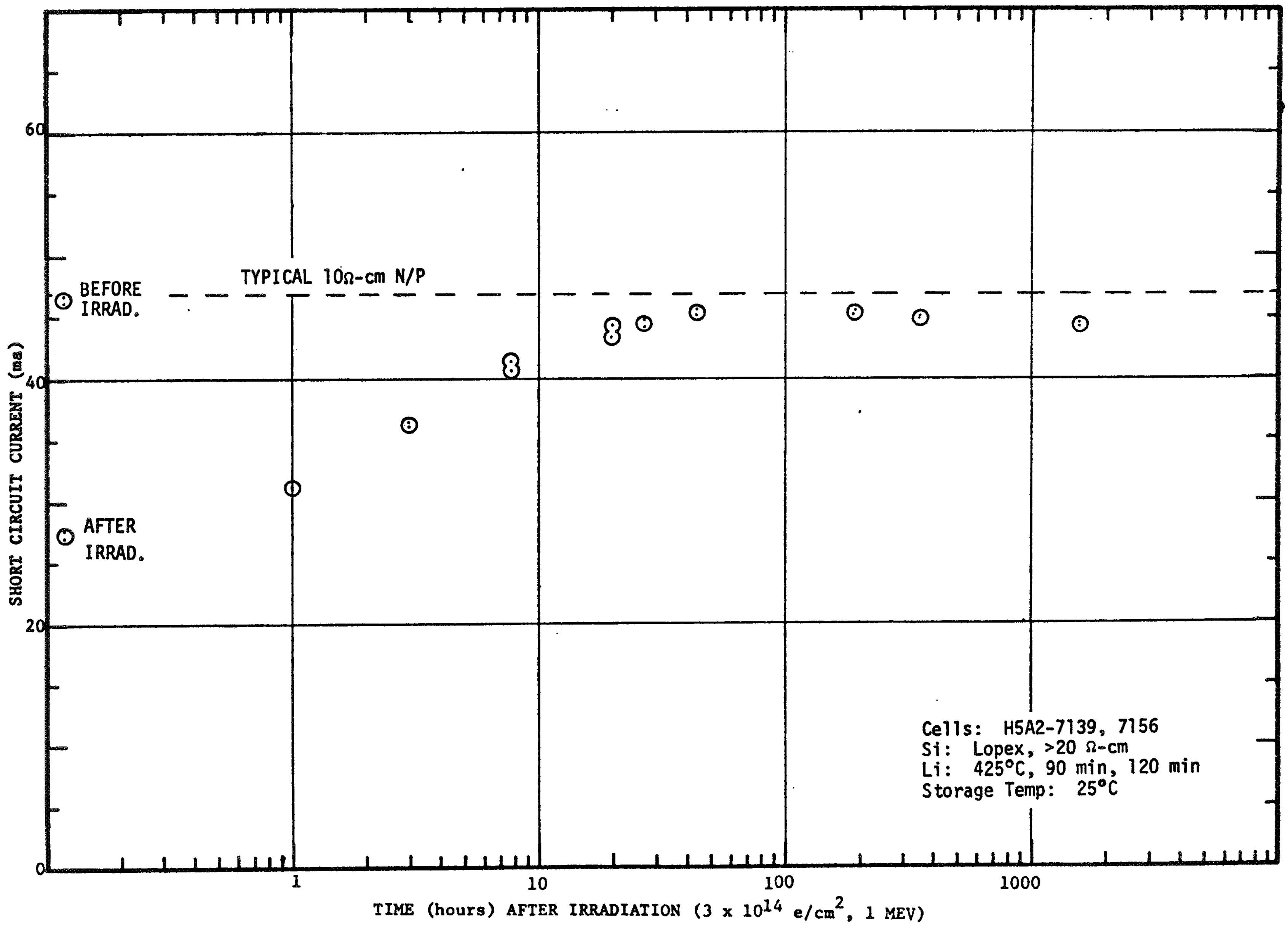

FIGURE 14 - RECOVERY OF GROUP H5A2 SOLAR CELLS, 3×10^{14} e/cm^2

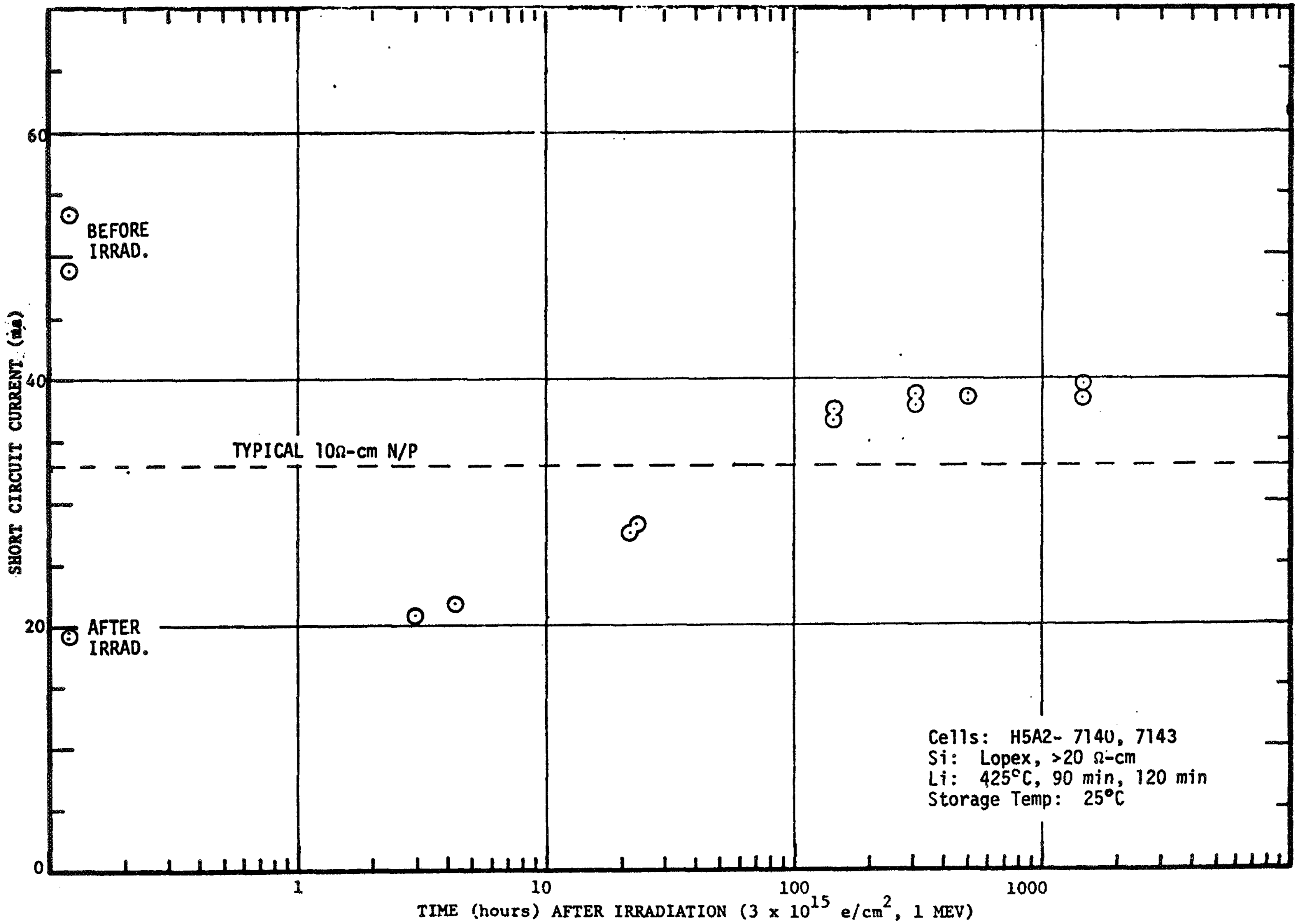

FIGURE 15 - RECOVERY OF GROUP H5A2 SOLAR CELLS, $3x10^{15}$ e/cm^2

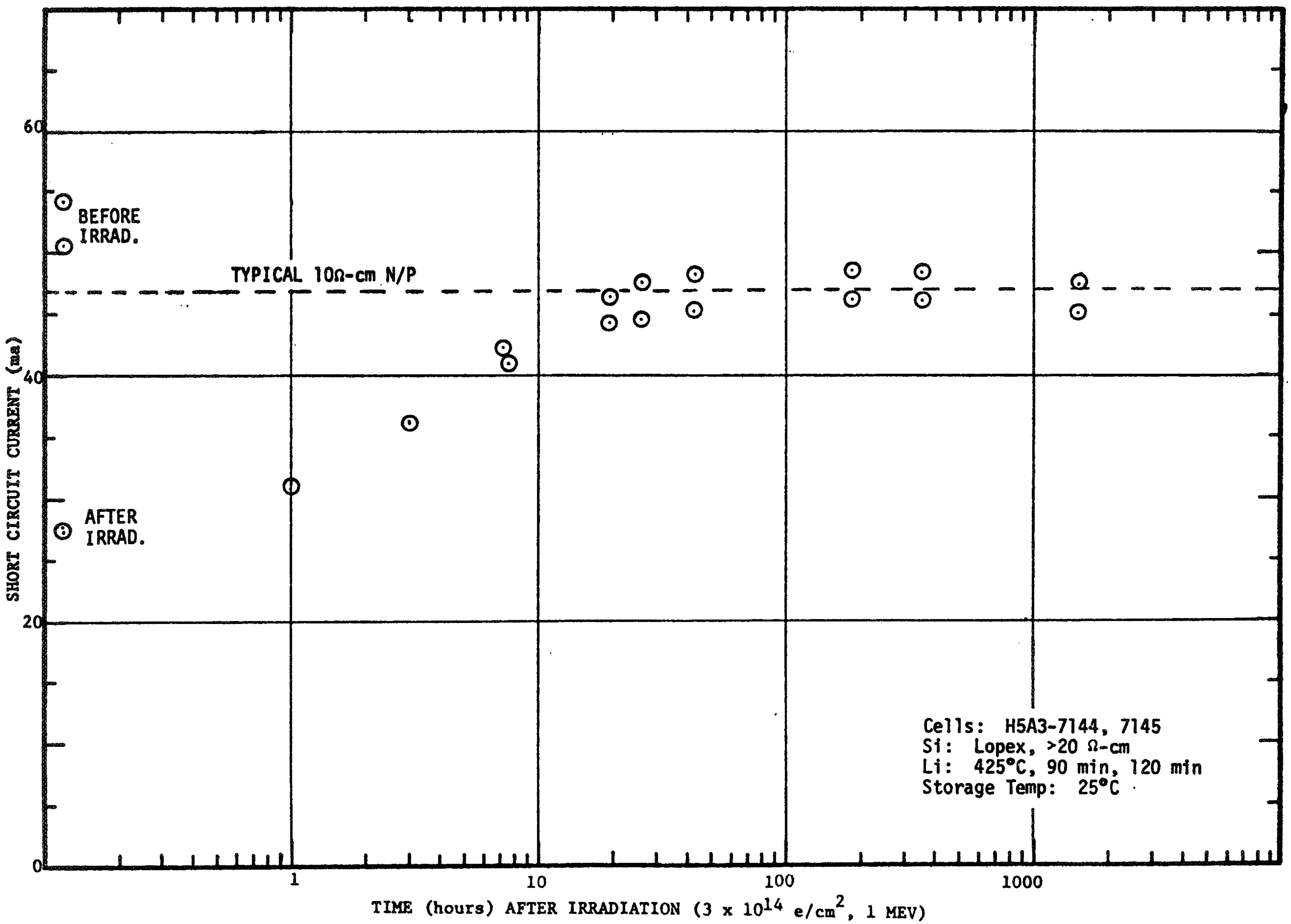

FIGURE 16 - RECOVERY OF GROUP H5A3 SOLAR CELLS, $3x10^{14}$ e/cm^2

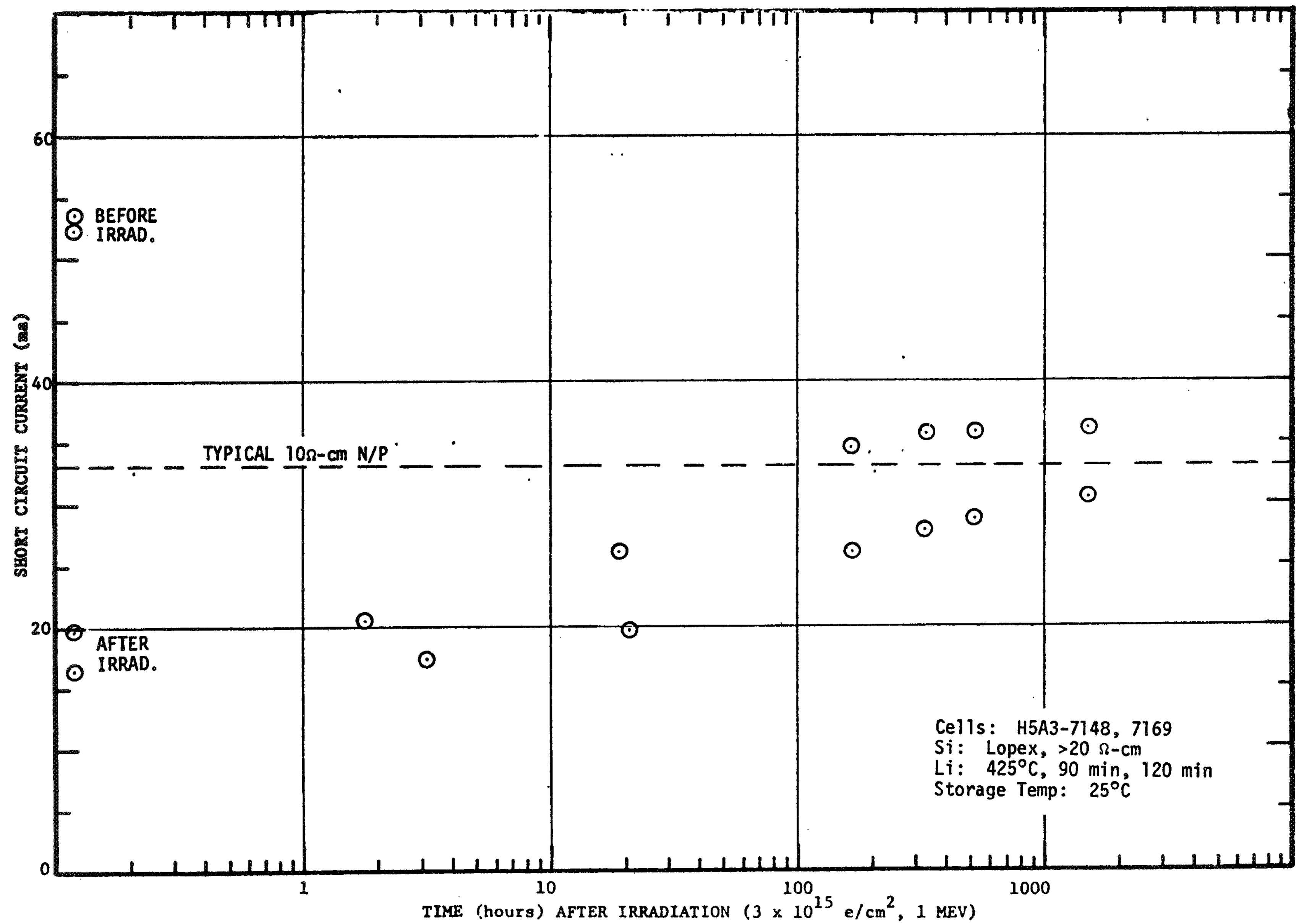

FIGURE 17 - RECOVERY OF GROUP H5A3 SOLAR CELLS, 3×10^{15} e/cm^2